

Investigations of the reasons for fungal durability of heat-treated beech wood

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Abstract

It is generally accepted that thermal treatment of wood by mild pyrolysis (retification or torrefaction) improves its durability to fungal degradation. However, this property has recently been questioned in the literature and definitely needs further investigation. The increase in durability conferred by thermal treatment is generally explained by four hypotheses: the low affinity of heat-treated wood to water; the generation of toxic compounds during heating; the chemical modification of the main wood polymers and the degradation of hemicelluloses. This study was undertaken to understand the reasons for durability of heat-treated beech wood. In order to confirm or not the above mentioned hypotheses, the durability of heat-treated beech wood towards *Coriolus versicolor* was evaluated according to different parameters like mass loss, wettability or chemical composition. The heat treatment was carried out in a temperature range of 20–280 °C under inert atmosphere for 10 different temperatures. The results show clearly an important correlation between the temperature of treatment and the fungal durability. At the same time, there was insufficient evidence to support the hypothesis of improved decay resistance due to generation of fungicidal compounds or due to the hydrophobic character of wood. Finally, the most plausible hypothesis to explain improvement of wood durability concerns its chemical modifications. Indeed, degradation of hemicellulose associated with other chemical modifications appearing during treatment could be the origin of improved durability. There is a good correlation between decay resistance and mass loss measurements which are directly correlated to hemicellulose degradation.

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1. Introduction

Beech is an important European softwood species widely used in the wood industry. However, its natural durability is too low for hazard class III, justifying the recourse to biocides for outdoor applications. Conventional wood preservation systems generally involve

impregnation of broadly active biocides into the wood [1]. However, these techniques are under increasing scrutiny with respect to their environmental impact, which may limit their scope of applications in the future [2]. Furthermore, the increasing environmental pressures over the last years in many European countries led to an important change in the field of wood preservation particularly in regard to the biocides toxicity, leading to the development of non-biocidal alternatives. Among these alternatives, heat treatment of wood, by mild pyrolysis, has been intensively investigated to increase

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its durability [3,4]. According to literature [5,6], the improved durability of heat-treated wood against fungi can be explained by four different reasons:

- an increase of the hydrophobic character of wood, which limited the sorption of water into the material and which is not favorable to the growth of fungi.
- generation of new extractives during heat treatment which can act as fungicides.
- modification of the wood polymers leading to a non-recognition of the latter by enzymes involved in fungal degradation.
- significant degradation of the hemicelluloses, which constitute one of the main nutritive source for fungi.

The aim of this paper is to investigate the effect of heat treatment on wood durability and to provide some evidence for its improved durability. To avoid problems of variability and reproducibility due to conditions of production of heat-treated wood (origin, size, time of treatment, temperature, etc.) encountered in different literature studies, we have chosen to perform our treatments in controlled conditions using different temperatures of heating and fixed residence time (8 h).

2. Materials and methods

Beech (*Fagus sylvatica*) heartwood was used throughout this study. Wood samples (blocks or sawdust) were oven dried at 80 °C until stabilization of their mass (approximately 48 h) before determination of their anhydrous weights.

2.1. Heat treatment

Heat treatment was performed on wood blocks (20 × 10 × 30 mm in tangential, radial and longitudinal directions) in a reactor placed in an oven at different temperatures during 8 h under a nitrogen atmosphere. The oven temperature was increased by 20 °C min⁻¹ from ambient to the operating temperature. After the treatment, the temperature decreases automatically until 20 °C. Mass loss after heat treatment was calculated according to the formula:

$$ML (\%) = 100(m_0 - m_1)/m_0$$

where m_0 is the initial oven dried mass of wood sample and m_1 is the oven dried mass of the same sample after heat treatment.

2.2. Evolution of extractives during heating

Extractives quantities before and after heat treatment were estimated by gravimetric measurements after

extraction. The extraction was performed on sawdust obtained after milling of the blocks by two consecutive extractions of 1.40 h with an ASE 200 Dionex extractor (35 bar) using hexane followed by toluene/ethanol mixture (2/1, v/v) as solvents. Extractives mass was determined after evaporation of the solvent under vacuum and weighing. At the same time, extractions were also performed on blocks using the same procedure to evaluate the effect of extractives on decay resistance.

2.3. Contact angle measurements

The use of contact angle measurements to determine the hydrophobic character of heat-treated wood has been presented in a preceding paper [7]. Wood wettability was measured by the Wilhelmy method according to a reported procedure [8,9]. Wood plates for θ_a determination (20 × 10 × 1 mm in tangential, radial and longitudinal directions) were obtained by mechanical sawing. The measuring unit was a tensiometer processor K12, Krüss society, Hamburg, Germany.

2.4. Biological trials

Extracted or unextracted dried blocks (20 × 10 × 30 mm in tangential, radial and longitudinal directions) were used for fungal durability evaluations. Petri dishes (9 cm diameter) were filled with sterile culture medium (20 ml) prepared from malt (20 g) and agar (40 g) in distilled water (1 l), inoculated with *Coriolus versicolor* and incubated at 22 °C and 70% HR to allow colonization of the medium by the mycelium. Extracted or unextracted blocks (three replicates) were placed in separate Petri dishes and exposed to fungus for 16 weeks to evaluate influence of the treatment and of the extractives on durability. Each experiment was duplicated. After this period, mycelia were removed and the blocks were dried at 80 °C and weighed (m_2) to determine the mass loss caused by the fungal attack.

$$ML' (\%) = 100(m_2 - m_3)/m_2$$

where m_2 is the initial oven dried mass of wood block before attack and m_3 is the oven dried mass after attack.

3. Results and discussion

3.1. Evolution of extractives during heating

Fig. 1 presents the evolution of the quantity of extractives during heat treatment measured either on massive wood or on sawdust obtained after crushing the wood blocks. The extracts quantities are generally slightly more important on sawdust than on bulk wood.

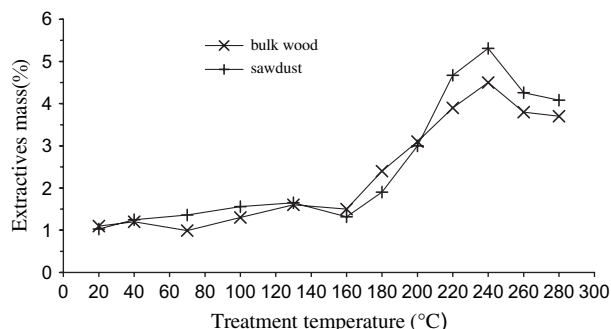


Fig. 1. Extractive mass generation of beech wood during heat treatment.

This result is caused by the difference of exchanging surfaces between bulk and crushed wood which favours mass transfer. However, this difference is slight and the technique is considered to ensure the absence of extractives in extracted wood blocks used for evaluations concerning the influence of extracts on fungal durability. The first part of the curves corresponds to the natural extractives present in beech (about 1%). Generation of extractives begins at 160 °C and becomes significant at temperatures higher than 200 °C. This behaviour was in a great part due to the beginning of hemicelluloses decomposition [5,10–13]. An optimum of extractives generation (4.5–5%) is observed in both cases (bulk and crushed wood) at a temperature close to 240 °C. For higher temperatures, extracts quantities decrease which probably corresponds to thermal decomposition and/or evaporation of the latter.

3.2. Effect of extractives on wood durability

Weight losses after 16 weeks of exposure to *C. versicolor* are reported in Fig. 2. Extracted and unextracted beech blocks show significant weight loss for treatments performed at low temperatures, between 20 and 180 °C. Durability of wood blocks treated at temperatures above 180 °C increases considerably and

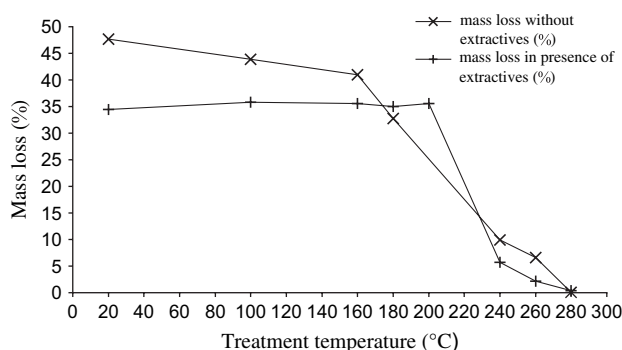


Fig. 2. Mass loss of beech wood block heat-treated after fungi attack.

for blocks treated at 280 °C, a total inhibition of fungal degradation is observed. In the first part of the curves, weight losses observed for extracted beech blocks are generally higher than those observed for unextracted blocks due certainly to the presence of natural extracts having some protective effects. However, these differences between extracted and unextracted blocks are very small and observed for practically all the experiments independently of the treatment temperature indicating that generation of extractives during heating had no effect on wood decay resistance. Consequently, it is possible to conclude that extracts generated during heating especially significant at 240 °C, have no effect on the durability. The same conclusions have been made by Kamdem et al. [6] who observed that industrial heat-treated pine, spruce and poplar extracted or not with water, acetone or chloroform presented similar weight losses after exposure to different brown rot or white rot fungi.

3.3. Effect of wettability on wood durability exposed to fungal degradation

The advancing contact angle and the mass loss obtained for beech blocks are presented in Fig. 3. Beech wood is totally wetted by water before heat treatment ($\theta_a = 0^\circ$). After heat treatment, in the temperature range between 130 and 160 °C, the wood wettability changes suddenly and the contact angle reaches the average value of 90°. For higher treatment temperatures between 160 and 260 °C wood keeps its hydrophobic character with $\theta_a = 90^\circ$ confirming similar observations reported in a previous study [14] using industrial heat-treated wood. Correlations between wettability and durability are not clear. Indeed, the hydrophobic character, which appears at 160 °C and which limits the sorption of water in the wood, has no influence on wood durability. Fungal degradation remains important for blocks treated at temperatures between 160 and 200 °C, even if the latter shows no water affinity. According to these results, the hypothesis, concerning

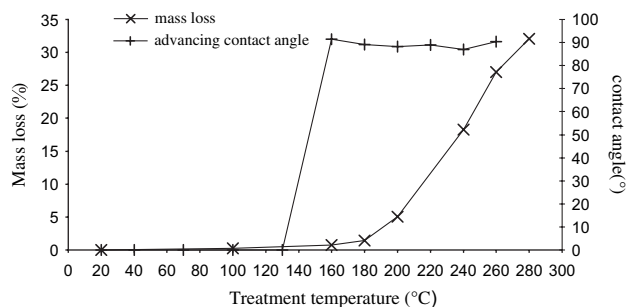


Fig. 3. Mass loss of beech wood and contact angle during the heat treatment.

the relation between hydrophobic character of wood and growth of fungi, cannot be retained. Similar observations have also been reported by Kamdem et al. [6] who reported that lower moisture content measured in wood after heat treatment are not connected to higher durability to fungi. Gosselink et al. [15] also reported that even if the water uptake of carbonised wood is lower than that of untreated wood when conditioned at 50 or 90% RH, the values obtained by immersion in water are quite similar, which lets us suppose that wood moisture content and malt agar medium are likely to be similar.

3.4. Effect of chemical modification on wood durability exposed to fungal degradation

Evolution of chemical composition of wood during heat treatment has been reported by us and in several other publications [10–13]. Any noticeable mass evolution was observed (Fig. 3) for temperatures between 80 and 180 °C, while, when the temperature is above 180 °C mass loss increases progressively to reach 32% at 280 °C. Mass losses can be explained mainly by hemicellulose degradation. Comparison of curves corresponding to mass losses due to fungal and thermal degradation as a function of heat treatment temperature indicates some similarities. Indeed, durability of heat-treated beech wood begins to increase at 200 °C when mass loss due to thermal degradation begins. For higher treatment temperatures, durability is inversely proportional to the observed mass losses due to thermal degradations. From these results, it is obvious that there is good correlation between the durability and wood polymers degradation caused by heat treatment. However, these results do not allow us to choose between the two latter hypotheses concerning either the degradation of hemicelluloses, considered as an important nutritive source for fungi, or the modification of the wood polymer network leading to its non-recognition by fungal enzymes.

Different studies show that thermal modification and degradation of wood components appear mainly for temperatures higher than 200 °C confirming the relation between durability and chemical modification. These modifications imply the degradation of hemicelluloses demonstrated by ¹³C NMR or FTIR analysis or chemical analysis involving Klason lignin determination and carbohydrate analysis but also modification of the lignin polymer network [5,10–12]. The fact that the white rot fungus *C. versicolor*, able to degrade lignin and polysaccharidic components of wood, is unable to attack beech wood treated at 280 °C seems to indicate that not only disappearance of hemicelluloses but also chemical modification of lignin is implicated in the increase of wood durability.

4. Conclusion

This study shows that heat treatment of beech wood increases its durability against the white rot fungus *C. versicolor*. The decay resistance depends on the treatment temperature and is total for treatments performed at 280 °C. Wettability changes observed during the heat treatment do not allow us to explain enhanced wood durability, especially for blocks treated between 160 and 200 °C, which show a significant hydrophobic character but are strongly degraded by *C. versicolor*. At the same time, heat-treated beech wood extracted or not exhibits quite similar mass losses indicating that extractives generated during heating are not at the origin of wood durability. The important correlation observed between the treatment temperature and the durability, indicates that chemical modification and degradation, which have been reported in the literature to appear above 200 °C, is the most plausible hypothesis to explain wood durability improvement. In addition to the important degradation of hemicelluloses, which are generally considered as an important nutritive source for the development of wood rotting fungi, modification of lignin network should also be involved to explain the ineffectiveness of fungal peroxidases to degrade lignin.

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